Office of Technology Development
TTP Summary

Title: INSITU CHEMICAL REMEDIATION OF RADIONUCLIDES IN SOILS

TTP No.: RF121101
Revision: 1
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Operation Office: Rocky Flats
Contractor: EG&G Rocky Flats, Inc.
Division: Technology Development

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Jointly Funded Program:	Yes
Integrated Demonstration:	GS06, In-situ Remediation
Primary Technology Area:	06-Soil Treatment
WBS Element:	DD01-14328
B&R Code:	EW4020

Task Summary

This proposed TTP constitutes Task 2 of the existing EM-50 funded TTP for Plutonium in Soils Integrated Demonstration Sampling Support. This task will conduct proof-of-principle, bench-scale evaluations of chemically enhanced steam stripping for the mobilization and removal of radioactive contaminated soils. The goal is to provide an *in situ* soil extraction process which uses chemically enhanced steam injection to mobilize and remove radionuclides — especially, plutonium and americium — from contaminated RFP soil. This effort is part of the treatability studies for remedial screening and selection process for actinide contaminated soils in Operable Unit No. 2 at the 903 Pad.

The objectives of this task are as follows:

- To characterize the physical and chemical conditions of soils that are contaminated with plutonium and americium. This includes clay mineralogy of *in situ* materials.
- To evaluate the effectiveness of chelating agents such as EDTA and citrate under steam injection conditions on the mobilization/removal of plutonium and americium in the OU 2/903 Pad soils.
- To select/obtain plutonium-contaminated subsurface soils from the 903 Pad area for lab studies and bench-scale tests.
- To perform bench-scale tests to evaluate mobilization of plutonium and americium using chelating agents under suitable redox conditions that simulate *in situ* conditions.
- To perform bench-scale tests to evaluate plutonium and americium mobilization/removal efficiency caused by chemically-enhanced steam injection conditions.

Steam injection technology has been demonstrated by Lawrence Livermore National Laboratory (LLNL) for remediating non-aqueous phase liquid (NAPL) and volatile organic compounds (VOCs) in subsurface soils and clay layers. This steam injection process accelerates removal of the NAPL contaminants and is combined with electrical heating methods. At Rocky Flats, we are interested in adapting the steam injection and electrical heating technologies by combining steam with chemical redox and complexing agents to remediate subsurface soils containing the radionuclides plutonium, americium, and uranium.

At the RFP site, there are several below-ground locations that are contaminated with VOCs and radionuclides (plutonium, americium, uranium). The phase II remedial investigation has detected contaminating plumes which contain radionuclides and VOCs. Contaminating media include soils and groundwaters. The radionuclide contamination includes plutonium, americium, and uranium. Metals contamination includes beryllium, cadmium and chromium. VOC contamination includes primarily trichloroethylene (TCE), carbon tetrachloride (CCl4), tetrachloroethane (PCE), chloroform, methylene chloride; cutting oils and lathe coolants. A schematic diagram of the 903 Pad area is shown in Figure 1.

Altering the steam injection temperature and pressures and concentration of the redox conditions and chelating agents, the plutonium and americium solubility will be increased significantly (10-100 times), thus facilitating the plutonium and americium mobility and subsequent collection within a contaminated soil. The steam front acts as a driving force to push the mobilized actinides to a collection well.

Bench-Scale Experiments:

Bench-scale experiments will investigate the various redox and chelating agents and establish optimum conditions for the *in situ* removal of radionuclides from subsurface soils. This approach will be used for the remediation of radionuclides (plutonium and americium) from the contaminated soil using a selective chelating agent prior to a field demonstration at 903 Pad. Bench-scale test results will demonstrate the best redox and chelating agents for mobilizing Pu and Am, help understand the process, and develop the basis for the pilot-scale test design.

This proposed TTP is Task 2 of the existing EM-50 funded TTP for Plutonium in Soils Integrated Demonstration Sampling Support. Six Subtasks form the basis of this proposed TTP.

These subtasks are:

Subtask 1. Design bench-scale tests.
Subtask 2. Conduct field sampling activities at the 903 Pad
Subtask 3. Perform bench-scale tests with different redox-chelating agents

Follow-on subtasks include:

Subtask 4. Design Conceptual pilot scale
Subtask 5. Prepare Final design and install Pilot-Scale Test.
Subtask 6. Perform Pilot-Scale demonstration at the 903 Pad area

Funding Schedule:

This TTP provides $380K in FY93 for Subtasks 1, 2 and initiation of Subtask 3 (bench-scale tests). FY93 funding for limited lab testing will be provided by LANL under Uranium in Soils Integrated Demonstration. LLNL will provide limited FY93 funds under the proposed TTP for peer review. Portions of Subtask 3 will likely be carried over to FY94. Subtasks 4, 5 and 6 will be carried out in FY94/95.

Budget Summary (Dollars in Thousands):

Sub Task	FY93	FY94
1. Design bench scale tests (workplan)	$70	
2. Conduct field sampling activities of the 903 Pad	$30	
3. Perform Bench-Scale Tests*	$280	
TOTAL	$380	**

* The $50K will be used by RFP to purchase bench-scale equipment and will probably be costed in early FY94.
** Actual expenses as of June 30, 1993 were $38K and commitment of a total of $90K is expected by EOY. Remaining funding will be carried over to FY94.

Task/Milestone Summary: FY 93	Date Complete
a. Bench-scale work/test plan and selection of chelating agents	8-2-93
b. RFP soil samples delivered to LANL	8-13-93
c. Status on the bench-scale tests (Letter report)	9-30-93

Milestone Explanation:

a. A bench-scale work plan will be developed which follows EPA Guide (EPA/540/R-92/071a) and describes redox conditions and chelating agents to be used to extract radionuclides, especially plutonium and americium under steam conditions. The work plan will also describe how the subsurface conditions at the 903 Pad area are modeled/simulated in the bench-scale tests. Data quality objectives and quality control/assurance requirements shall be included, per requirements of scientific notebooks.

b. Collection and delivery of RFP contaminated soil samples to LANL. This includes the selection, collection, and shipment to LANL of subsurface and/or representative soil samples from the 903 Pad area. The bench-scale studies then begin as Task 3. These will be performed jointly by LANL and RFP with additional testing anticipated in FY94 and will continue into FY94.

c. Letter Report- A letter report describing bench scale experiment results and interim conclusions will be issued by 9/30/93. This report will provide sufficient details and information to substantiate continuing this TTP to the subsequent phases including a Pilot-Scale Evaluation of technology in the field.

Subtask Description:

Subtask 1. Bench-Scale Work Plan.

This task will prepare a work plan for bench-scale testing which follows "Suggested Organization of Treatability Study Work Plan" in EPA's *Guide on Conducting Treatability Studies under CERCLA* (EPA/540/R-92/071a) including sections on: Project Description, Treatment Technology Description, Test Objectives, Experimental Design and Procedures, Equipment and Materials, Sampling and Analysis, Data

Management, Data Analysis and Interpretation, Health and Safety, Residuals Management, Community Relations, Reports, Schedule, Management and Staffing, and Budget. The work plan will also define the applicability of the bench-scale test results in mimicking the subsurface conditions at the 903 Pad area.

A summary of the available literature on plutonium in soils studies performed at RFP will be included. Background information will be summarized and include the physical setting, geochemistry and geology, subsurface contaminants radionuclides and VOCs distribution in soils. If required an evaluation of the need for further characterization or analytical data, and paper study of the various chelating (complexing) agents for radionuclides (Pu and Am) will be added.

This task will also include completing, as required, operational safety analysis plan (OSA), job safety analysis (JSA) plan, health and safety (H&S) plan, and standard operating procedures for the bench-scale tests for handling radioactivity and performing radioactive experiments prior to starting any bench-scale experiments at RFP.

Subtask 2. Field Activities of the 903 Pad Area

This task will identify, based on past RFP OU 2 work, and sample surface soils from locations which ensure sample representiveness. Soil will be collected and handled according to LANL or RFP procedures. The soil will be screened for radioactivity levels to ensure adherence to H&S radiological protection constraints before transferring to LANL/TA-48 or Bldg 881 for bench-scale tests.

Subtask 3. Bench-Scale Testing

Bench-scale testing will be a significant collaboration between RFP and LANL in FY94. A majority of FY93 laboratory work will be performed at LANL to meet the accelerated schedule. FY94 treatability tasks will be coordinated and completed at both RFP and LANL in a joint effort. We will investigate the effectiveness of various redox and chelating agents that will mobilize plutonium and americium under steam conditions (near 100°C). Since plutonium solubility and chemistry varies with oxidation state, various reducing/oxidizing conditions will be evaluated for their impact on mobilizing plutonium. We will also investigate the stability of chelating agents under steam conditions.

A systematic study to establish optimum conditions with the various chelating agents is also crucial in deciding whether to proceed further for Subtasks 4 through 6. Because of the large number of tests involved, some tests will be performed at LANL some bench tests will be performed at RFP. The RFP radiochemistry lab in Bldg. 881 will perform additional bench-scale experiments and support the pilot-scale testing program.

Subtask 4. Conceptual Pilot-Scale Design (FY94)

This subtask will produce a conceptual pilot-scale design for the field operation. The design is anticipated to include chemically enhanced steam injection and associated feed and support subsystems, process control and monitoring technology, and any effluent collection and treatment subsystems. The steam injection system will take advantage of existing steam service or will include a boiler (6 months lease), piping, fuel, tanks, etc. Approximately 12 to 16 extraction/injection wells will be installed in the 903 Pad area.

Subtask 5. Review and Analysis Assessment (FY94)

This subtask will conduct safety analyses, risk assessments, and evaluation of safety design of equipment to be used in the conceptual design (Task 4) and field demonstration (Task 6). Plans and procedures for operations including S/O testing will be completed.

Subtask 6. Pilot Test / Field Demonstration (FY95)

This task will conduct the actual field demonstration on the 903 Pad area.

Background:

Soil and groundwater contamination with trace amounts of plutonium and americium mixed with VOCs and dense NAPLs is an lingering problem in many remediation programs. Large volumes of contaminated soils may require processing to reduce contaminants to acceptable (often yet to be defined) levels. Concentrated VOC plumes are present in the clays and silt of Rocky Flats alluvium and in porespaces and fractures of sedimentary sandstones, siltstones, and claystones. The permeability of these geologic units permits the percolatation of these contaminant plumes and subsequent migration and eventual discharge of these contaminants as seeps into the surface waters.

There are various remediation technologies such as physical, chemical, biological, and thermal, that can be applied to effectively isolate the radionuclides and VOCs from groundwater and soils. Under the thermal category, one innovative technology is dynamic underground stripping (DUGS) — which is an adaptation of steam injection and direct electrical heating. The LLNL (Roger Aines and Robin Newmark) have successfully tested this technology on a bench scale and small field scale for the removal of NAPLs/VOCs in soils or clay layers at LLNL.

Methodology:

The main focus of this remediation study is contaminated soil from the 903 Pad (see Figure 1). Conceptually, using a direct electrical heating concept coupled with steam injection, the VOCs could be driven off and collected by a vacuum extraction technique. If the radionuclide contaminants such as uranium, plutonium, and americium could be mobilized (e.g., complexed with chelates such as EDTA and citrate) they could be removed as well. Removal will be more difficult if the radionuclides are concentrated in an inorganic matrix, making them relatively unavailable for this "leaching" technology.

The effectiveness of mobilization or removal will depend on the chemical associations of radionuclides. The underground conditions at RFP are moderately oxidizing, and thus uranium and plutonium are in the oxidized state (U+6 and Pu+4). If the radionuclides are associated with the NAPLs/VOCs, they may be removed. Uranium, being indigenous, is mostly concentrated in the silicate matrix, whereas, plutonium and americium is mostly adsorbed on the surface of silt and clay sized fractions, often associated with organic or Fe-based minerals. Further, the steam injection chemistry can be altered in terms of pH and Eh (using CO_2 partial pressure), where the plutonium and americium solubilities can be increased by factors of 10 to 100 times, and thus facilitating the plutonium and americium mobility from the contaminated soil. This proposed TTP combines these concepts and offers a novel approach to separate the radionuclides from VOCs, and then mobilize or remove plutonium from the contaminated soils of the 903 Pad.

Technical Progress/Milestone:

FY 93

1. Prepare Bench Scale Work Plan. This will be completed in early 8/93.
2. Deliver soil samples to LANL. This shall be completed by the middle of 8/93.
3. Issue letter report on the bench scale test progress. This will be completed by 9/30/93.

Funding Basis:

	FY93 ($K)	FY94 ($K)
FTE	1.0	**
Labor	330	
CE	50*	
Subcontract	0	
Total	380	**

* The $50K capital funding in FY93 will be used to purchase bench-scale equipment for the 881 Lab experiments and will be deferred to FY94.

** This is new TTP involving support from LANL, LLNL, and RFP and is expected to have a FY93 carryover; funding level for FY94 is expected to require an additional $350K.

Work Breakdown Structure Element:
This TTP shall be performed under PSWBS as an Environmental and Waste Management Technology Development RDDT&E program. The subprogram is entitled Supporting Technology Investment Areas. The Cost Account is Plutonium In Soils, and the Work Package is entitled Plutonium Integrated Demonstration Sample Support.

Technology Need:

Steam injection is an attractive technology for remediation of contaminated soils. This technology can be used to separate NAPLs/VOCs from a mixed wastes with radionuclides. Further, this technology can be extended and enhanced using redox chemistry and complexing agents to remediate radionuclides (plutonium, americium, and uranium) from contaminated soils. The proposed technology is a novel approach in remediating both the VOCs and radionuclides from a contaminated site such as the 903 Pad area at RFP site.

Alternatives:
Alternatives for remediating soils containing mixed waste includes excavation for treatment and replacement, or for packaging and disposal elsewhere, frequently resulting in very large volumes of waste requiring disposal elsewhere. This technology is capable of removing the contaminants on site, with a small volume of waste to be disposed of and no soil removal. Clean up costs of soils and ground water will be enormous and run into millions dollars

Benefits:

This approach uses relatively mild chemical conditions to a refractory remediation problem, and has high potential for *in situ* remediation. Additionally, the use of chemically enhanced steam/water and relatively mild conditions offers significant advantages over more aggressive chemical treatments such as acid or caustic leaching, which are inappropriate for *in situ* methods and also "sterilize" the soils treated. Steam injection can be used as an in-situ technology to mobilize radionuclide- and VOCs-contaminated soils with minimum generation of secondary waste streams. This technology provides enormous benefits in terms of reducing waste volumes. For example, at RFP 95% of the waste is a mixed (hazardous and radioactive) waste. The application of this technology can substantially reduce the volume of mixed waste and cost of remediation. Consequently, waste processing and disposal concerns are minimized.

Criteria For Success:
The success criteria for CESS bench-scale tests are based on the following performance goals:

- Has Pu and Am mobility in clay soils been achieved and maintained to allow for transfer from original deposition sites to a potential collection site.
- Determine the maximum potential for removing radionuclides from soils with chemically enhanced steam, e.g., 80% of radionuclides are removed.
- Determine the types, mobility, and levels of residual contaminants.
- Determine types,volumes, and levels of secondary waste streams.
- Will risk-based maximum contamination clean up levels be achieved, e.g., ARARS
- Have contaminant toxicity and volumes been significantly reduced.

Regulatory Requirements:
Secondary waste streams will be generated. These include gas emissions, surface water discharges, and some soil residues. Under the Interagency Agreement (IAG, EPA-State-DOE), the waste streams or the discharge effluent from a remediation process or a field demonstration must meet the regulatory requirements of discharge limits per the Clean Water Act (CWA); Safe Drinking Water Act (SDWA) 40CFR 141.11 to 141.16 for radionuclides and hazardous constituents. Discharge of all hazardous constituents and radionuclides will be monitored to ensure that all discharges are below the regulatory requirements.

Technology Transfer:

This technology will be evaluated and potentially extended to other DOE sites for remediating mixed waste and radionuclides (Pu, Am, U, Ra, etc.) from contaminated soils. The technology will also be available for transfer to the private sector.

Acceptability:

The principal investigators (E.H Wilson, J.C. Laul and K. M. Motyl) will work closely with DOE, EPA, and the State to ensure that the proposed studies are properly utilized on a DOE site for remediation of radionuclides, especially in field demonstration. RFP will ensure that the planned system designs (steam chemistry), operations of equipment, and effluent waste streams comply with the regulatory requirements.

Integrated Contractor Order:

Not required for FY93.

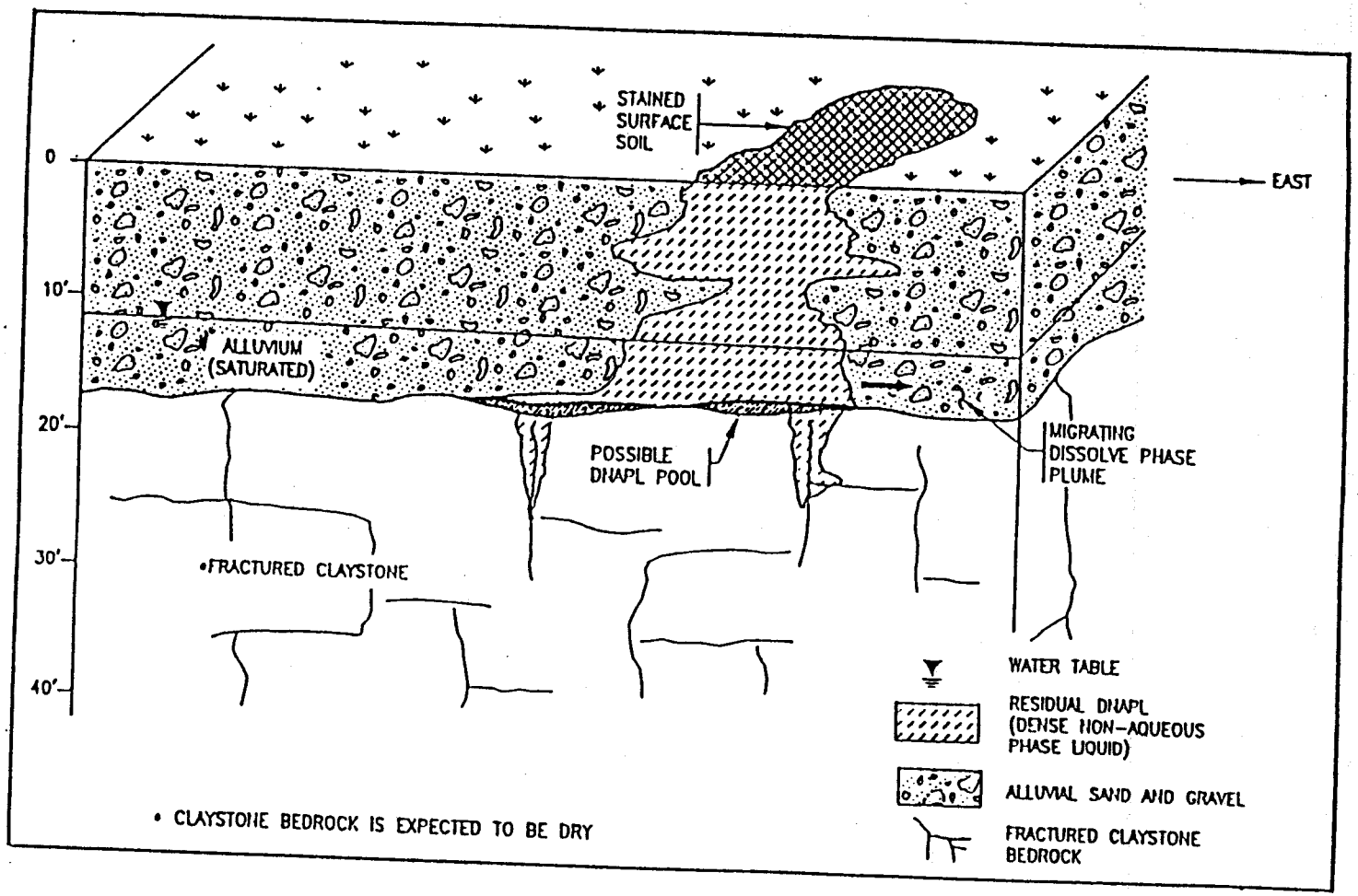

Figure 1. A Schematic Diagram of the 903 Pad Area.